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Chen et al.

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(54) **NANOCOMPOSITES WITH HIGH THERMOELECTRIC FIGURES OF MERIT**

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C22C 1/04 (2006.01)

(Continued)

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CPC **B29C 43/36** (2013.01); **Y10T 428/2938** (2013.01); **H01L 35/16** (2013.01); **H01L 35/22** (2013.01); **Y10S 257/00** (2013.01)

USPC **419/23**; 419/39; 419/48; 136/201; 136/238; 136/239; 136/240; 438/93; 438/95

(58) **Field of Classification Search**
USPC 419/42; 136/201, 239; 438/93
See application file for complete search history.

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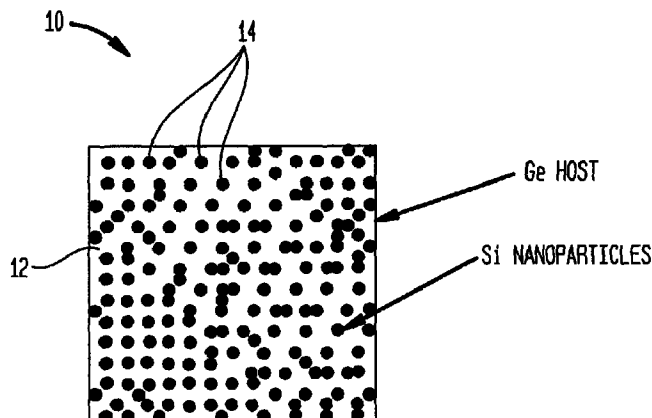
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(57) **ABSTRACT**

The present invention is generally directed to nanocomposite thermoelectric materials that exhibit enhanced thermoelectric properties. The nanocomposite materials include two or more components, with at least one of the components forming nano-sized structures within the composite material. The components are chosen such that thermal conductivity of the composite is decreased without substantially diminishing the composite's electrical conductivity. Suitable component materials exhibit similar electronic band structures. For example, a band-edge gap between at least one of a conduction band or a valence band of one component material and a corresponding band of the other component material at interfaces between the components can be less than about $5k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of said nanocomposite composition.

13 Claims, 8 Drawing Sheets



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FIG. 1

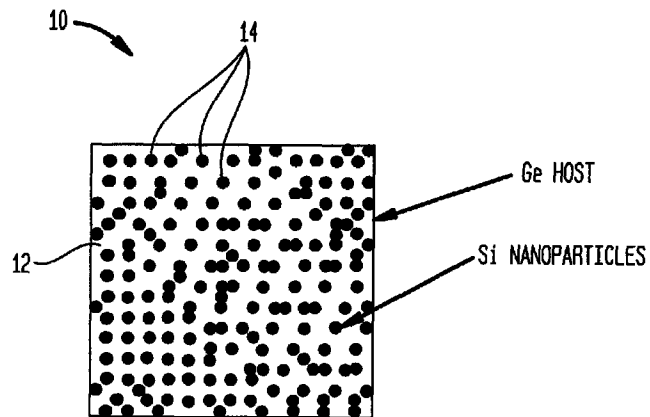


FIG. 2A

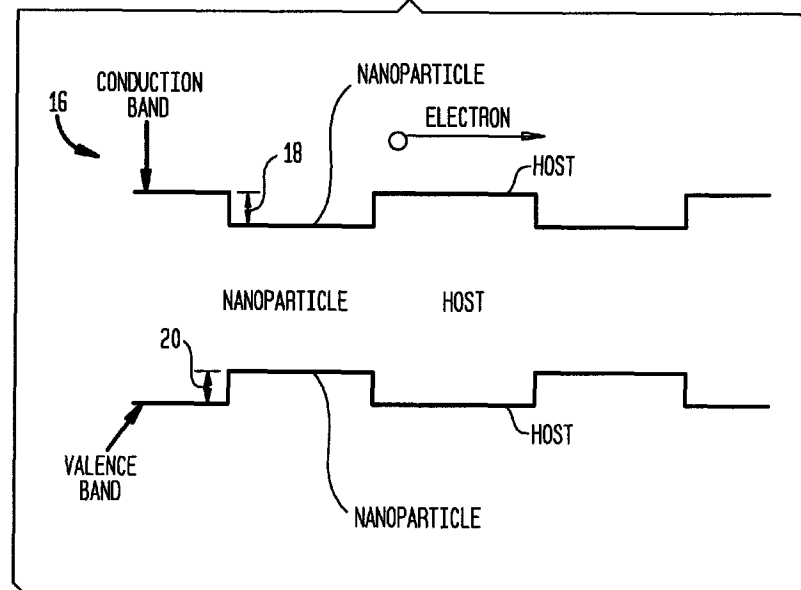


FIG. 2B

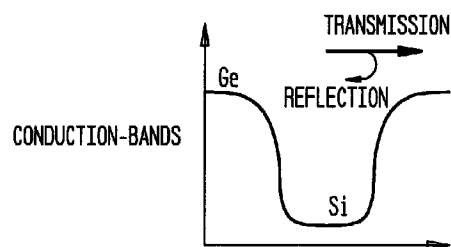


FIG. 3

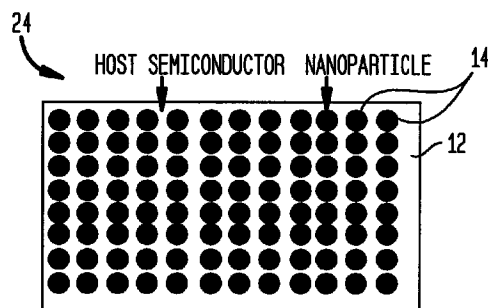


FIG. 4

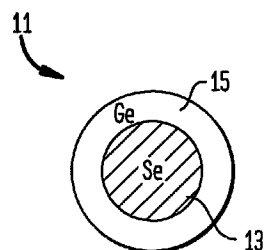


FIG. 5A

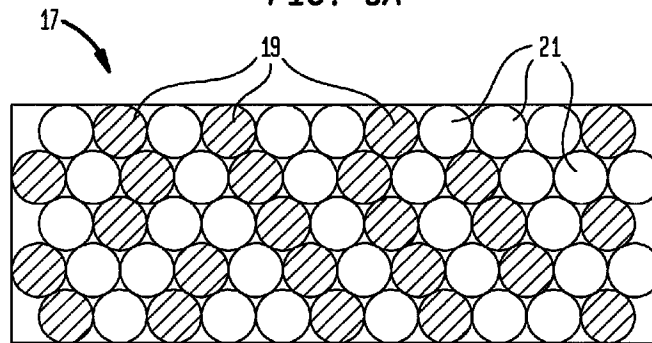
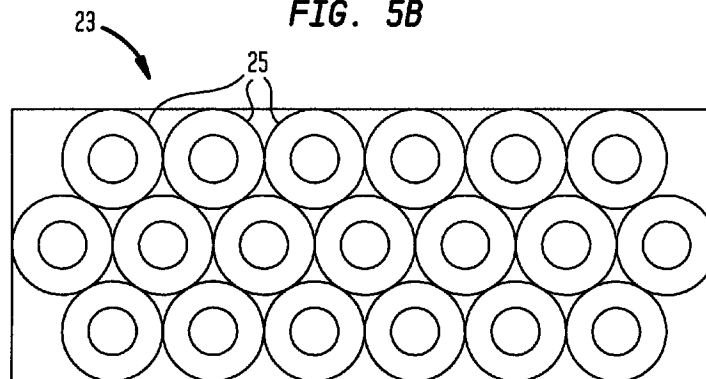
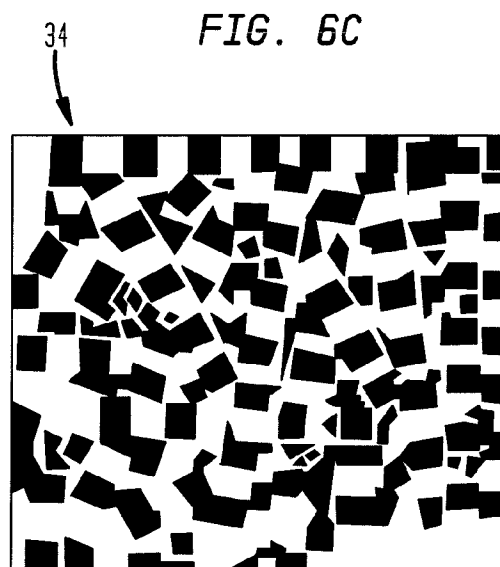
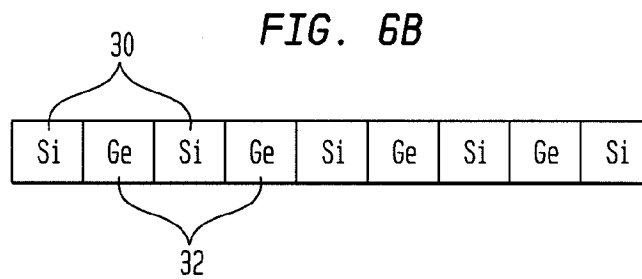
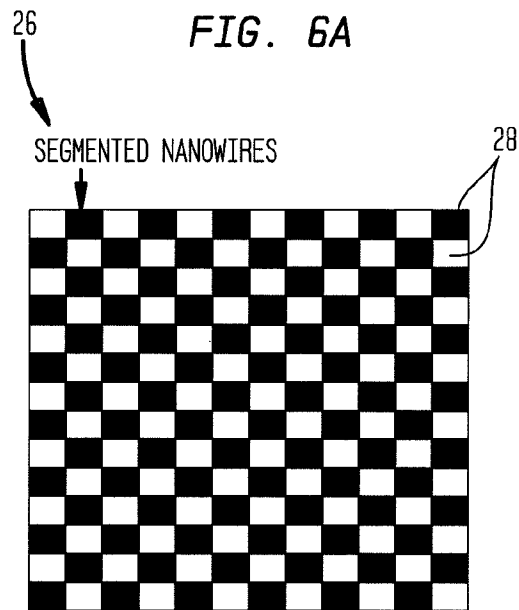
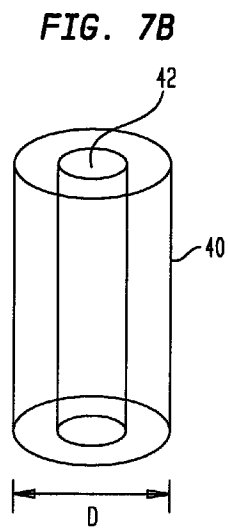
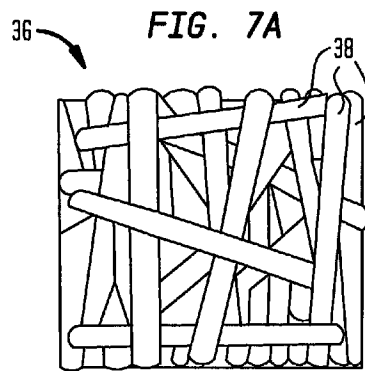
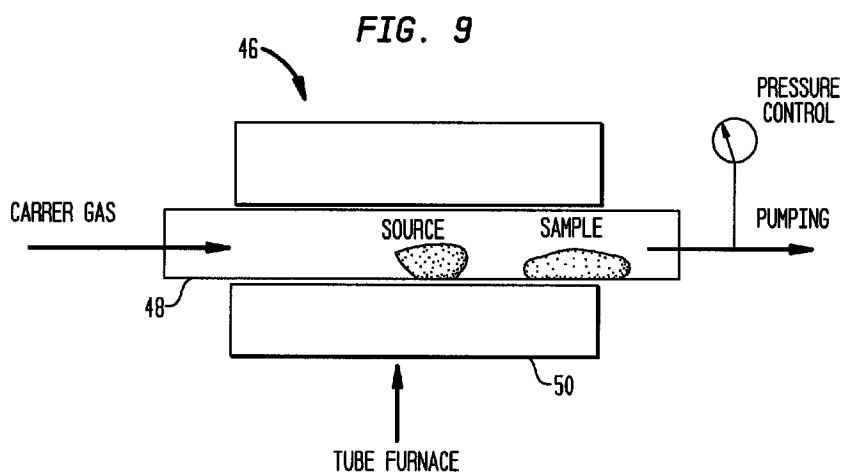
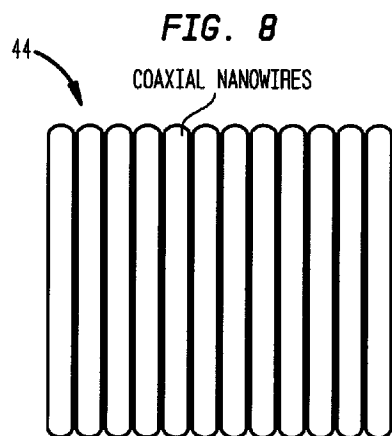


FIG. 5B









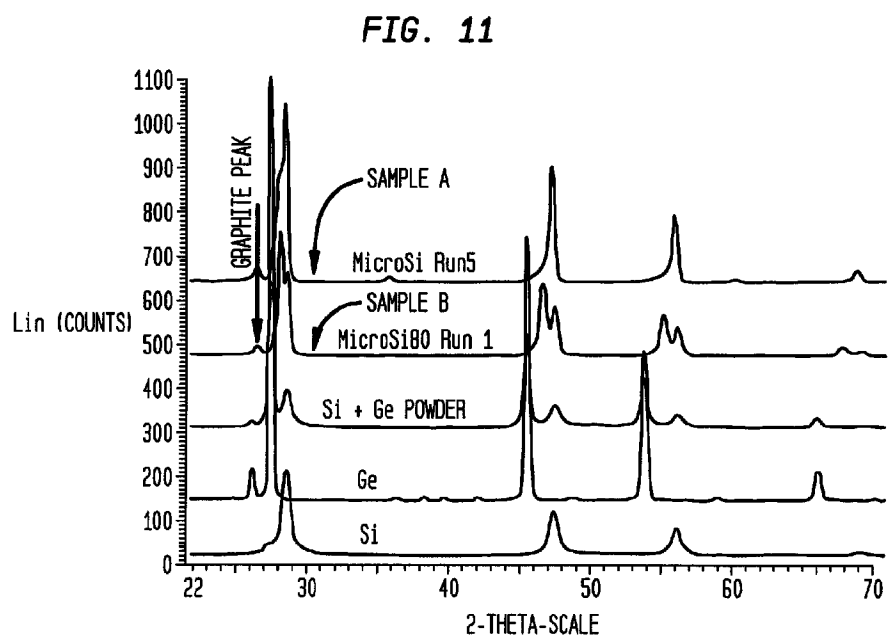
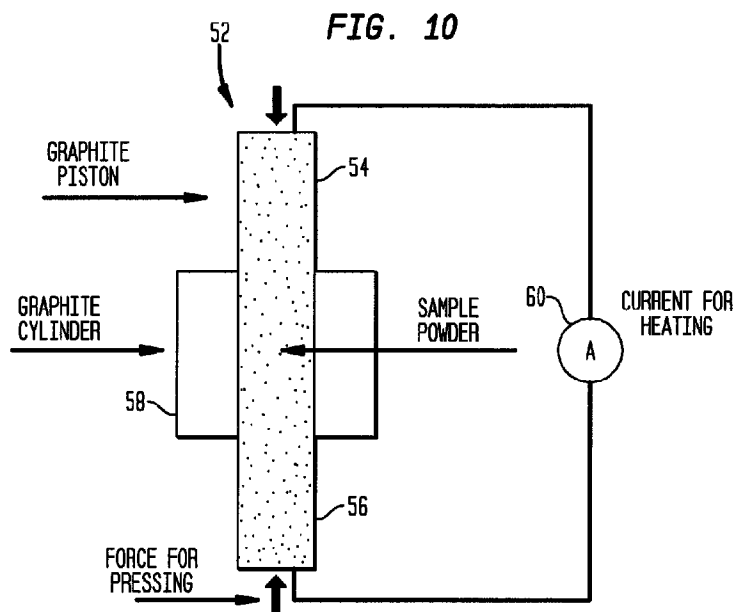


FIG. 12

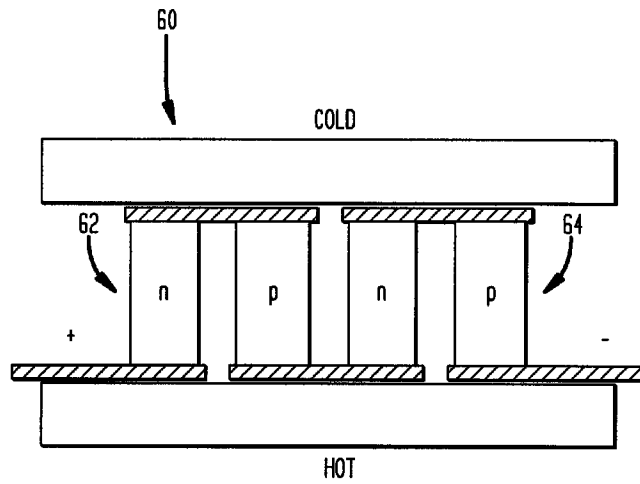
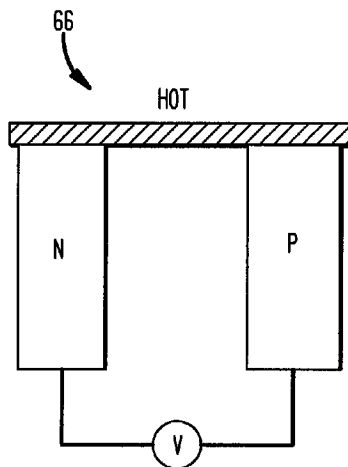


FIG. 13



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NANOCOMPOSITES WITH HIGH THERMOELECTRIC FIGURES OF MERIT

RELATED APPLICATION

This application claims priority as a continuation application to a utility application entitled "Nanocomposites With High Thermoelectric Figures of Merit" having a Ser. No. 12/273,783 filed on Nov. 19, 2008, which claims priority as a continuation application to a utility application entitled "Nanocomposites With High Thermoelectric Figures of Merit" having a Ser. No. 10/977,363 filed on Oct. 29, 2004 and patented as U.S. Pat. No. 7,465,871, both of which are incorporated by reference in their entireties.

FEDERALLY SPONSORED RESEARCH

This invention was made with government support under Grant No. NAS3-03108 awarded by NASA. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

The present invention is generally directed to thermoelectric materials and methods for their synthesis and, more particularly, to such materials that exhibit enhanced thermoelectric properties.

Solid-state cooling and power generation based on thermoelectric effects are known in the art. For example, semiconductor devices that employ Seebeck effect or Peltier effect for power generation and heat pumping are known. The utility of such conventional thermoelectric devices is, however, typically limited by their low coefficient-of-performance (COP) (for refrigeration applications) or low efficiency (for power generation applications). A thermoelectric figure-of-merit

$$(Z = \frac{S^2 \sigma}{k},$$

where S is the Seebeck coefficient, σ is the electrical conductivity, and k is thermal conductivity) is typically employed as the indicator of the COP and the efficiency of thermoelectric devices. In some cases, a dimensionless figure-of-merit (ZT) is employed, where T can be an average temperature of the hot and the cold sides of the device.

Applications of conventional semiconductor thermoelectric coolers are rather limited, as a result of a low figure-of-merit, despite many advantages that they provide over other refrigeration technologies. In power generation applications, low efficiency of thermoelectric devices made from conventional thermoelectric materials with a small figure-of-merit limits their applications in direct conversion of heat to electricity (e.g., conversion of waste heat or heat generated by specially designed sources).

Accordingly, there is a need for enhanced thermoelectric materials, and methods for their fabrication. More particularly, there is a need for thermoelectric materials exhibiting an enhanced figure-of-merit.

SUMMARY OF THE INVENTION

The present invention is generally directed to nanocomposite thermoelectric materials that exhibit enhanced thermoelectric properties. The nanocomposite materials include two or more components, with at least one of the components

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forming nano-sized structures within the composite material. The components are chosen such that thermal conductivity of the composite is decreased without substantially diminishing the composite's electrical conductivity. Suitable component materials exhibit similar electronic band structures. For example, a band-edge offset between at least the conduction bands or the valence bands of the two component materials can be less than about $5k_B T$, and preferably less than about $3k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition.

In one embodiment, the present invention provides a thermoelectric nanocomposite semiconductor composition that includes a plurality of nano-sized structures formed of a first selected semiconductor material, and a plurality of nano-sized structures formed of another semiconductor material intermixed together. The nanosized structures can be, for example, nanoparticles or nanowires. For example, the structures can be formed of two different types of nanoparticles having average diameters in a range of about 1 nm to about 1 micron, or preferably in a range of about 1 nm to about 300 nm, or in a range of about 5 nm to about 100 nm.

In another embodiment, the thermoelectric nanocomposite can include a semiconductor host material and a plurality of nano-sized inclusions (e.g., nanoparticles or nanowires), formed of a semiconductor inclusion material, that are distributed within the host material. The nanocomposite composition exhibits a band-edge offset between the conduction bands or the valence bands of the host material and the inclusion material at an interface that is less than about $5k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. For example, the band-edge offset can be in a range of about 1 to about $5k_B T$, or in a range of about 1 to about $3k_B T$. An energy minimum of the conduction band or the valence band of the inclusion material can be preferably less than an energy minimum of a corresponding band of the host material. Alternatively, the energy minimum of a conduction band or a valence band of the host material can be less than an energy minimum of a corresponding band of the inclusion material.

The terms "nano-sized structure" and "nano-sized inclusion," as used herein, generally refer to material portions, such as nanoparticles and nanowires, whose dimensions are equal or preferably less than about 1 micron. For example, they can refer to nanoparticles having an average cross-sectional diameter in a range of about 1 nanometer to about 1 micron, or in a range of about 1 nm to about 300 nm, or in a range of about 5 nm to about 100 nm. Alternatively, they can refer to nanowires having average transverse (cross-sectional) diameter in a range of about 2 nm to about 200 nm.

A variety of different materials can be employed to form the components of the nanocomposite composition. For example, one component (e.g., host material) can comprise PbTe or $PbSe_x Te_{1-x}$ (where x represents the fraction of PbSe in the alloy of PbTe and PbSe, and can be between 0-1) and the other (e.g., inclusion material) can comprise any of PbSe or $PbSe_y Te_{1-y}$. Alternatively, one component can comprise $Bi_2 Te_3$ and the other can comprise $Sb_2 Te_3$ or $Bi_2 Se_3$, or their alloys. In other embodiments, one component can be Si and the other Ge. For example, Si inclusions can be embedded in a Ge or a SiGe alloy host. In another example, the host and the inclusion materials can be formed of SiGe alloys having different relative concentrations of Si and Ge in the host material than in the inclusion material. Those having ordinary skill in the art will appreciate that other materials can also be employed so long as their material properties conform with the teachings of the invention.

In another aspect, the semiconductor component materials (e.g., nano-sized inclusions) can be randomly distributed within the composite. Alternatively, the components can be distributed according to a pattern. Further, one or more components (e.g., the host material or the inclusion material, or both) can be doped with a selected dopant, for example, an n-type or a p-type dopant, with a concentration of, e.g., about 1 percent. In some embodiments that employ Si and Ge materials, boron is utilized as a p-type dopant while phosphorous is employed as an n-type dopant. Those having ordinary skill in the art will appreciate that other dopants can also be employed.

In further aspects, the nanocomposite semiconductor material can exhibit a reduction in thermal conductivity relative to a homogeneous alloy formed of the component materials by a factor of at least about 2, e.g. a factor in a range of about 2 to about 10. Further, the nanocomposite material can exhibit a thermoelectric figure of merit (ZT) that is greater than 1. For example, the figure of merit can be in a range of about 1 to about 4.

In another aspect of the invention, the nanocomposite composition exhibits an electrical conductivity (σ) that differs, if at all, from an electrical conductivity of a homogeneous alloy formed of the component materials by a factor less than about 4. While in some cases the nanocomposite semiconductor can exhibit an electrical conductivity that is less than that of the homogeneous alloy, in other cases the electrical conductivity of the nanocomposite composition can be greater than that of the homogeneous alloy. The Seebeck coefficient, S , of the nanocomposites can be comparable or greater than that of the homogeneous alloy. Further, the power factor, defined as $S^2\sigma$, can be comparable or greater than that of the homogeneous alloy.

In another embodiment, the invention provides a thermoelectric nanocomposite material that comprises a plurality of nanowires of a first type formed of a selected semiconductor material intermixed with a plurality of nanowires of a second type formed of another semiconductor material. The interfaces between the two types of nanowires exhibit a band-edge discontinuity in any of a conduction band or a valence band that can be less than about $5k_B T$, or preferably less than about $3k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. For example, one type of nanowires can be formed of Ge while the other type is formed of Si. While in some embodiments, the nanowires of the first and second types are randomly disposed relative to one another, in other embodiments they are disposed in a three-dimensional pattern relative to one another.

In yet another embodiment, the present invention provides a nanocomposite material formed of a plurality of stacked nanowire structures. Each nanowire structure can comprise an outer shell formed of one semiconductor material and an inner core formed of another semiconductor material, where an interface of the outer shell and the inner core exhibits a band-edge discontinuity between any of a conduction band or a valence band of the outer shell and a corresponding band of the inner core that is less than about $5k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. The outer shell and inner core can form a coaxial nanowire structure having an average diameter in a range of about 2 nm to about 200 nm. For example, the core can be formed of Si and the shell of Ge, or vice versa.

In other aspects, the invention provides a thermoelectric nanocomposite semiconductor composition that includes a semiconductor host material and a plurality of nano-sized

inclusions, formed of a semiconductor inclusion materials, that are distributed within the host material, where a band-edge offset between at least one of a conduction band or a valence band of the host material and a corresponding band of the inclusion material at an interface with the host material is less than about 0.1 eV.

In another aspect, the present invention provides a method of synthesizing a thermoelectric nanocomposite semiconductor composition that includes generating a powder mixture comprising two sets of nano-sized semiconductor structures, and applying a compressive pressure to the mixture while heating it at a temperature and for a time duration chosen to cause compaction of the two sets of nano-sized structures into a nanocomposite material. The compressive pressure can be, for example, in a range of about 10 to about 1000 MPa. Another way to make the nanocomposites is to add nanoparticles or nanowires with higher melting point into a melt of the host material and agitate the mixture through, for example, induction heat caused fluid mixing.

In a related aspect, compression can be enhanced by heating the mixture, e.g., by causing a current density flow through the compressed mixture for heating thereof. In general, the current level (e.g., current density) can depend on the sample size. In some embodiments, a current density in a range of a few thousands A/cm² (e.g., 2000 A/cm²) can be employed.

Further understanding of the invention can be obtained by reference to the following detailed description in conjunction with the associated drawings, which are briefly described below.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically depicts a thermoelectric nanocomposite composition in accordance with one embodiment of the present invention,

FIG. 2A schematically depicts variations of electronic band-edge offset at interfaces of the host and the inclusion materials in the nanocomposite composition of FIG. 1,

FIG. 2B is a graph illustrating that an energy minimum of the conduction band of n-doped silicon nanoparticles embedded in a germanium host material can be lower (depending on the stress conditions) than the energy minimum of the germanium host's conduction band,

FIG. 3 schematically depicts a thermoelectric nanocomposite composition according to another embodiment of the invention in which a plurality of nanoparticles are distributed according to a three-dimensional pattern in a host,

FIG. 4 schematically depicts a nanoparticle having a core portion formed of one semiconductor material surrounded by a shell formed of another semiconductor material,

FIG. 5A schematically depicts a thermoelectric nanocomposite material according to another embodiment of the invention, which is formed as a mixture of two types of semiconductor nanoparticles,

FIG. 5B schematically depicts a nanocomposite material according to one embodiment of the invention that includes a plurality of semiconductor nanoparticles having core-shell structures,

FIG. 6A schematically depicts a thermoelectric nanocomposite material according to another embodiment of the invention, which is formed of a stack of segmented nanowires,

FIG. 6B is a schematic cross-sectional view of a segmented nanowire of the composition of FIG. 6A,

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FIG. 6C schematically depicts a thermoelectric nanocomposite material according to another embodiment of the invention, formed as plurality of randomly stacked segmented nanowires.

FIG. 7A schematically depicts a thermoelectric nanocomposite material according to another embodiment of the invention, formed of a plurality of randomly stacked coaxial nanowires.

FIG. 7B is a schematic perspective view of a coaxial nanowire of the nanocomposite material of FIG. 7A.

FIG. 8 schematically depicts a thermoelectric nanocomposite material formed of a plurality of coaxial nanowires disposed in a three-dimensional pattern relative to one another.

FIG. 9 schematically illustrates a vapor phase deposition system for generating nanoparticle and nanowires.

FIG. 10 schematically illustrates a plasma compaction apparatus suitable for synthesizing a thermoelectric nanocomposite material from a mixture of nanoparticles.

FIG. 11 presents X-ray diffraction data corresponding to two prototype nanocomposite samples according to the teachings of the invention as well as a silicon sample, a germanium sample, and a sample composed of a powder mixture of silicon and germanium.

FIG. 12 schematically depicts a thermoelectric cooler formed as a cascade of thermoelectric modules fabricated by employing thermoelectric nanocomposite materials of the invention, and

FIG. 13 schematically depicts a thermoelectric device for converting heat to electricity.

DETAILED DESCRIPTION

The present invention is generally directed to thermoelectric nanocomposite materials, and methods for their fabrication, that generally include a mixture of semiconductor nano-sized structures, or semiconductor nano-sized inclusions embedded in a semiconductor host, that provide a heterogeneous composition. The semiconductor materials are selected so as to substantially preserve electron transport properties of the nanocomposite material relative to the host or a putative homogeneous alloy formed of the semiconductor components while the heterogeneity of the composition enhances phonon scattering, thereby resulting in an enhanced thermoelectric figure-of-merit, as discussed in more detail below.

With reference to FIG. 1, a thermoelectric semiconductor composition 10 according to one embodiment of the invention includes a host semiconductor material 12 (e.g., Ge or SiGe alloy), herein also referred to as a host matrix, in which a plurality of nano-sized inclusions 14 (e.g., Si or SiGe alloy of a different Ge concentration than a host also formed of a SiGe alloy) are embedded. In this embodiment, the exemplary inclusions are in the form of substantially spherical particles having average diameters in a range of about 1 nm to about 300 nm, or more preferably in a range of about 1 nm to about 100 nm, which are distributed randomly within the host matrix. It should be understood that the shape of the nanoparticles 12 is not limited to spherical. In fact, they can take any desired shape. Further, while in some embodiments, the interfaces between the nanoparticles and the host can be sharp, in other embodiments, an interface can include a transition region in which the material composition changes from that of the host to that of the inclusion.

The nanoparticles 14 are formed of a semiconductor material, herein also referred to as an inclusion material, that has an electronic band structure that is similar to that of the host material, as discussed in more detail below. In this exemplary

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embodiment, the host material comprises germanium or SiGe alloy while the inclusion material is silicon or SiGe alloy. Alternatively, germanium nanoparticles can be embedded in a silicon host. Both the host material and the inclusion material can be doped with a dopant, e.g., an n-type dopant or a p-type dopant. In general, the doping concentration can be optimized for different materials combinations. In some embodiments, the doping concentration can be, for example, about 1 percent. In other embodiments, the host material can be any of SiGe, PbTe, or Bi₂Te₃ while the inclusion material can be any of PbSe, PbSeTe or Sb₂Te₃, or vice versa. Other suitable materials can be PbSn, or alloys of PbTeSeSn. Group III-V materials can also be utilized, such as InSb matched to another material or other materials in accordance with the teachings of the invention to other III-V materials. Other examples include HgCdTe system, Bi and BiSb system. Those having ordinary skill in the art will appreciate that other host and inclusion materials can also be employed so long as their electronic and thermal properties conform to the teachings of the invention, as described in more detail below.

In general, the host and the inclusion materials are selected such that a band-edge offset between the conduction bands or the valence bands of the host material and the inclusion material at an interface of the two materials is less than about $5k_B T$, and preferably less than about $3k_B T$, wherein k_B is the Boltzmann constant and T is an average temperature of the nanocomposite composition. For example, the band-edge gap can be less than about 0.1 eV.

The concept of a band-edge offset between two adjacent semiconductor materials is well known. Nonetheless, for further elucidation, FIG. 2A presents a schematic graph 16 illustrating variation of the conduction band and the valence band energies, and more specifically the changes associated with the minimum energy of the conduction band and the maximum energy of the valence band, at interfaces of the host material and the inclusion material in an exemplary thermoelectric semiconductor composition according to some embodiments of the invention, such as the above semiconductor composition 10. The conduction band energies are offset by an amount 18 while the valence band energies are offset by an amount 20 at interfaces of the host and inclusion materials. As noted above, in many embodiments, the offset 18 or 20, or both, are less than about $5k_B T$, wherein k_B is the Boltzmann constant and T is an average temperature of the nanocomposite composition. It should also be understood that in some embodiments the nanoparticles can have higher energy conduction bands, or lower energy valence bands, relative to the host so long as energy offsets remain small, e.g. within about $5k_B T$. Such small band-edge offsets lead to small potential barriers facing electrons at interfaces of the host and the inclusion materials, thereby minimizing electron scattering at these interfaces. In this manner, the electrical conductivity of the nanocomposite composition remains close to that of a putative homogeneous alloy formed from the host and the inclusion materials. For example, the electrical conductivity of the nanocomposite can differ, if any, from that of the putative homogeneous alloy by a factor less than about 4 and in some instances by a factor of 3 or 2. While in many embodiments, the electrical conductivity of the nanocomposite composition is less than that of the putative alloy, in some cases, it can be greater.

In some embodiments, the host and the inclusion materials are selected such that the energy extrema of either the inclusion material's conduction band or its valence band, or both, are lower than the extremum energy of a corresponding band of the host material. For example, FIG. 2B presents a graph schematically depicting that the conduction band energy of

n-doped silicon nanoparticles embedded in a germanium host material can be lower than the conduction band energy of the germanium host.

Although the nanoparticles in the above thermoelectric composition **10** are randomly distributed within the host matrix **12**, in a nanocomposite composition **24** according to another embodiment of the invention, shown schematically in FIG. **3**, the nanoparticles **14** are embedded in the host matrix **12** in accordance with a regular three-dimensional pattern.

In some embodiments of the invention, the nanoparticles **12** are composed of a core formed of one semiconductor material and a shell surrounding the core, which is formed of another semiconductor material. By way of example, FIG. **4** schematically depicts one such nanoparticle **11** having a silicon core **13** and a germanium shell **15**. Alternatively, the core can be formed of an alloy, e.g., a silicon-germanium alloy, and the shell of a selected semiconductor material, such as germanium. In other embodiments, both the core and shell are formed of semiconductor alloys. For example, both the core and shell can be formed of SiGe alloy, but with different concentrations of Si relative to Ge.

FIG. **5A** schematically depicts a thermoelectric nanocomposite composition **17** according to another embodiment of the invention that includes nanoparticles of two types (e.g., formed of two different semiconductor materials) that are intermixed together. Similar to the previous embodiment, the materials of the two types of nanoparticles are chosen such that they exhibit substantially similar electron properties. More particularly, the materials are selected such that a band-edge offset between the conduction bands or the valence bands of the different particle types at interfaces thereof is less than about $5k_B T$, or preferably less than about $3k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. For example, a plurality of nanoparticles **19** (depicted with dashed lines) can be formed of Si while the remaining nanoparticles **21** are formed of Ge. In other embodiments the nanoparticles **19** and **21** can be formed of SiGe, PbTe, PbSe, PbSeTe, Bi_2Ti_3 or Sb_2Te_3 . For example, one nanoparticle type can be formed of PbSe and other of PbSeTe. Those having ordinary skill in the art will appreciate that other semiconductor materials can also be employed for forming the nanoparticles **19** and **21** so long as their material properties conform with the teachings of the invention. Although in FIG. **5A**, for ease of illustration, the nanoparticles of the two types are shown as substantially spherical with the nanocomposite exhibiting some spatial gaps, in many embodiments of the invention the nanoparticles are densely packed together potentially resulting in some distortions of the particles shapes, relative to isolated state, and disappearance of the spatial gaps.

In many embodiments, one or both types of nanoparticles are doped with a selected dopant, e.g., an n-type or p-type dopant. Although the nanocomposite composition **17** is formed of two types of nanoparticles, in other embodiments, a mixture of more than two types of nanoparticles can also be employed. As noted above, the material properties of the nanoparticles are selected such that the differences, if any, among their electronic band structures are minimal.

In some embodiments, the nanoparticles **19** or **21**, or both, can be a core-shell structure such as that shown in FIG. **4** above. For example, the particles **19** can be formed of a silicon core surrounded by a germanium shell. With reference to FIG. **5B**, in another embodiment, a nanocomposite composition **23** is formed of a mixture of nanoparticles **25** that are compacted together, where each nanoparticle has a heterogeneous structure, e.g., a core-shell structure such as that shown in FIG. **3** above. For example, each nanoparticle can have a

silicon core and a germanium shell. Alternatively, each nanoparticle can include a SiGe core surrounded by a Si or Ge shell or SiGe alloy with a different composition.

A nanocomposite thermoelectric material accordingly to the teachings of the invention, such as the above compositions **10** and **17**, advantageously exhibit an enhanced thermoelectric figure-of-merit (Z) which can be defined as follows:

$$Z = \frac{S^2 \sigma}{k}$$

where S is the well-known Seebeck coefficient, σ is the electrical conductivity of the composite material, and k is its thermal conductivity. The figure-of-merit Z has the units of inverse Kelvin. In many cases, a dimensionless figure-of-merit (ZT), obtained as a product of Z and an average device temperature (T), is employed. A nanocomposite thermoelectric composition according to the teachings of the invention, such as the compositions **10** and **17**, can exhibit a thermoelectric figure-of-merit (ZT) that can be greater than about 1. For example, it can exhibit a thermoelectric figure-of-merit in a range of about 1 to about 4, or in range of about 2 to about 4. For example, it can exhibit a ZT greater than about 1 at room temperature (about 25 C).

Without being limited to any particular theory, the enhanced thermoelectric properties of nanocomposite materials of the invention can be understood as being due to a reduction in phonon thermal conductivity while concurrently preserving electron transport properties. For example, in the thermoelectric nanocomposite material **10** described above, the interfaces between the nano-sized inclusions and the host material can cause an increase in phonon scattering, thereby reducing the thermal conductivity of the nanocomposite material. However, the small band-edge offset between the host and the inclusion materials minimizes electron scattering at these interfaces. Even with a small reduction of electrical conductivity, the Seebeck coefficient can be increased such that $S^2 \sigma$ would be comparable, or even greater than that of a homogeneous alloy formed of the host and inclusion materials. Such a combination of electron-phonon transport properties can lead to a better thermoelectric figure-of-merit, as can be readily corroborated by reference to the definition of Z above. Particularly, the interfaces between the nanoparticles in the above nanocomposite composition **17** can lead to a lowering of thermal conductivity of the composite relative to a putative homogenous alloy formed of the materials of the two nanoparticle types while small differences between the electronic band structures of the two materials can substantially preserve electron transport properties.

In addition, the thermoelectric nanocomposite materials of the invention can exhibit enhanced power factors, which can be defined as follows:

$$\text{power factor} = S^2 \sigma$$

where S is the Seebeck coefficient, and σ is the electrical conductivity of the composite material. For example, power factors in a range of about 2×10^{-4} W/mK² to about 100×10^{-4} W/mK² can be obtained. Without being limited to any particular theory, the power factor enhancement can be due to quantum size effects exhibited by the nano-sized components of the thermoelectric compositions.

Thermoelectric nanocomposite compositions according to the teachings of the invention are not limited to those described above. By way of example, FIG. **6A** schematically illustrates a thermoelectric nanocomposite composition **26**

according to another embodiment of the invention that includes a plurality of segmented nanowires **28** that are compacted, in a manner described in more detail below, to form a nanocomposite material. With reference to FIG. 6B, each segmented nanowire can include segments **30** formed of one type of semiconductor material interleaved with segments **32** formed of another type of a semiconductor material. For example, the segments **30** can be formed of silicon while the segments **32** are formed of germanium. Those having ordinary skill in the art will appreciate that other semiconductor materials can also be employed for forming these segments. In this exemplary embodiment, the segmented nanowires can have cross-sectional diameters in a range of 1 nm to about 300 nm, and more preferably in a range of about 1 nm to about 20 nm. In general, similar to the previous embodiments, semiconductor materials of the segments **30** and **32** are selected so as to minimize differences between their electronic band structures. More specifically, in many embodiments of the invention, a band-edge offset between the conduction bands or the valence bands of the semiconductor material of the two segment types, at an interface of the two materials, is less than about $5k_B T$, and preferably less than about $3k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. For example, the band-edge gap can be less than about 0.1 eV.

Although the segmented nanowires **28** in the above nanocomposite composition **26** are disposed relative to one another in a regular three-dimensional pattern, in another embodiment **34**, shown schematically in FIG. 6C, the nanowires **28** are randomly located relative to one another.

FIG. 7A schematically illustrates a thermoelectric nanocomposite composition **36** according to another embodiment of the invention that is formed of a plurality of stacked nanowire structures **38**, each of which is composed of two nanowires disposed substantially coaxially relative to one another. For example, as shown schematically in FIG. 7B, each nanowire structure **38** can include an outer shell **40** formed of a semiconductor material that surrounds an inner core **42**, which is formed of another semiconductor material. The coaxial nanowire **38** can have a cross-sectional diameter D in a range of about 1 nm to about 1 micron, or in a range of about 1 nm to about 300 nm, and more preferably in a range of about 1 nm to about 100 nm.

The semiconductor materials for forming the nanowire structures **38** are selected such that an interface of the outer shell and the inner core would exhibit a band-edge offset between conduction bands or the valence bands of the outer shell and corresponding bands of the inner core less than about $5k_B T$, wherein k_B is the Boltzman constant and T is an average temperature of the nanocomposite composition. For example, the band-edge gap can be less than about 0.1 eV.

The heterogeneity of the nanocomposite composition **36**, e.g., the interfaces between the outer shells and the inner cores of the nanowire structures forming the composition, can increase phonon scattering, thereby reducing the composition's thermal conductivity. The electrical conductivity is, however, less affected because the semiconductor materials of the outer shells and the inner cores are chosen so as to minimize differences between their electronic band structures. In other words, the heterogeneity of the composition can affect phonon scattering without substantially altering electron transport properties, thereby resulting in enhanced thermoelectric properties of the composition.

Although in the above thermoelectric composition the nanowire structures include two layers—an inner core surrounded by an outer shell—in other embodiments, more than two layers, e.g., two coaxially disposed shells surrounding an

inner core, can be employed. Further, although the coaxial nanowires **38** in the above composition **36** are disposed randomly relative to one another, in another embodiment **44**, shown schematically in FIG. 8, the coaxial nanowires are arranged relative to one another according to a three-dimensional pattern.

A variety of techniques can be employed to fabricate thermoelectric nanocomposite compositions according to the teachings of the invention, such as those described above. In general, known techniques, such as, wet chemistry techniques and vapor-liquid-solid condensation, can be utilized to generate the nanostructures, e.g., nanoparticles or nanowires. These nanostructures are preferably incorporated within a host material, or intermixed with one another, while taking precautions to avoid generation of interface states, e.g., interface oxides, that could contribute to electron scattering, as discussed in more detail below. For example, silicon nanoparticles can be treated in an HF solution to remove any SiO_2 coating formed thereon.

In one method, a host material is impregnated with nanoparticles by taking advantage of a difference between the melting temperature of the host and that of the nanoparticles. For example, nanoparticles can be embedded within a host material having a lower melting point than that of the nanoparticles. Some illustrative examples of such nanoparticles and host materials include: Si nanoparticles embedded in a Ge host, PbSe nanoparticles inside a PbTe host, and Sb_2Te_3 nanoparticles inside a Bi_2Te_3 host. Dopants can also be incorporated into the host and the nanoparticles. In some embodiments, dopants can be directly added to the host. More preferably, dopants can be added to the nanoparticles in addition to the host.

In many fabrication techniques, nanoparticles and nanowires are utilized as building blocks for generating nanocomposite materials according to the teachings of the invention. Hence, exemplary methods for generating some exemplary nanoparticles as well as nanowires are described below. Those having ordinary skill in the art will appreciate that similar techniques can be utilized for forming nanoparticles and nanowires of other materials.

In many embodiments of the invention, nanoparticles, such as Si or Ge nanoparticles, are synthesized by employing wet chemistry or vapor deposition techniques. Both water-based and non-water-based wet chemistry techniques can be employed. By way of example, Ge nanocrystals can be synthesized by utilizing a low temperature inverse micelle solvothermal method—a non-water-based technique—that is capable of yielding gram quantity of Ge nanocrystals. The preparation of Ge nanoparticles can be performed, for example, in a Parr reactor (e.g., model 4750, Parr Company, Moline, Ill., USA). A typical exemplary procedure for preparing Ge nanospheres can be as follows: 80 mL of hexane, 0.6 mL of GeCl_4 , 0.6 mL of phenyl- GeCl_3 , 0.6 mL of pentaethylene glycol monododecyl ether (C12E5), and 5.6 mL of Na (25 w % dispersion in toluene) can be added to a 200 mL flask. This mixture can be stirred for about 30 minutes, for example, via a magnetic stirrer, and subsequently transferred to a Parr reactor. The Parr reactor can be kept at an elevated temperature, e.g., at 280 C, for about 72 hours in a furnace without stirring or shaking and then cooled to room temperature.

Germanium nanospheres can then be obtained from a black powder collected at the end of the above process by washing the powder with excess amounts of hexane, alcohol, and distilled water in order to remove any NaCl byproducts and hydrocarbon residue. This can be followed by a drying step performed, e.g., in an oven, at 60 C for about 12 hours.

Experimental characterizations of prototype Ge nanoparticles synthesized by the above procedure indicate these particles have crystalline structure and nanometer sizes, e.g., a diameter of about 20 nm. A similar approach can be utilized for synthesizing silicon nanoparticles. In preferred embodiments, the above synthesis steps are preferably performed under an inert atmosphere, e.g., an atmosphere of argon, so as to inhibit formation of surface oxide layers that can degrade thermoelectric properties of nanocomposite materials generated by employing the nanoparticles, as discussed in more detail below.

The above wet chemistry approach can also be utilized to form nanoparticle having a core portion surrounded by a shell, such as the above nanoparticle 11 shown schematically in FIG. 4. For example, a nanoparticle having a germanium core and silicon shell can be synthesized by forming Ge core first, and subsequently the Si shell in Ge- and Si-containing solution respectively.

As another example, PbSe nanoparticles can be synthesized by utilizing a water-based wet chemistry protocol described briefly below. For example, in one embodiment, 50 milliliter of water can be mixed with 50 mg of a surfactant, e.g., PEG, and 1.3 grams of sodium hydroxide (NaOH). To this mixture, 78 mg of Se and 378 mg of lead acetate, i.e., $\text{Pb}(\text{CH}_2\text{COOH})_2 \cdot 3\text{H}_2\text{O}$, can be added. This is followed by adding a reducing agent (e.g., $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) to the mixture while stirring it. The mixture can then be held in a pressure vessel at a temperature of about 100 C for about 18 hours, and the resultant material can be washed with water/ethanol to obtain PbSe nanoparticles having average diameters of about 28 nm. The above volumes and masses of different reagents are given for illustrative purposes, and those having ordinary skill in the art will appreciate that other values can also be employed.

In another example, PbTe nanoparticles can also be synthesized in a similar manner. For example, in one approach, 50 milliliter of water can be mixed with 50 mg of a surfactant, e.g., PEG, and 2.4 grams of sodium hydroxide (NaOH). To this mixture, 127 mg of Te and 420 mg of lead acetate, i.e., $\text{Pb}(\text{CH}_2\text{COOH})_2 \cdot 3\text{H}_2\text{O}$, can be added. This is followed by adding a reducing agent (e.g., $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) to the mixture while stirring it. The mixture can then be held in a pressure vessel at a temperature of about 160 C for about 20 hours, and the resultant material can be washed with water/ethanol to obtain PbTe nanoparticles having average diameters of about 10 nm. The above volumes and masses of different reagents are given for illustrative purposes, and those having ordinary skill in the art will appreciate that other values can also be employed.

In some cases, vapor phase deposition techniques can be employed for synthesizing nanoparticles and nanowires needed for fabricating nanocomposite materials according to the teachings of the invention. For example, in one approach, vapor phase deposition can be utilized for synthesizing Si nanowires and nanoparticles. For example, FIG. 9 schematically illustrates a system 46 for synthesizing Si nanowires and nanoparticles via vapor phase deposition, which includes a graphite boat 48 with one small opening at each end thereof that is placed in a furnace 50. A source material, e.g., silicon monoxide or silane gas (SiH_4) (e.g., 99.5%), is disposed at a higher temperature end of the boat. The system can then be evacuated to a low pressure, e.g., 0.01 Torr, by a pump, e.g., a rotary pump, and a flowing carrier gas (e.g., argon with high purity mixed with 50% hydrogen) can be introduced into the boat from one end. In this exemplary embodiment, the gas flow rate is selected to about 100 sccm and the pressure is kept at about 100 Torr. Those having ordinary skill in the art will

appreciate that other gas flow rates can also be employed. The system can be heated to about 1350 C at the source position and held at this temperature for about one hour. The gas flow carries vapor from the source downstream portion of the tube to be deposited on a substrate, e.g., a silicon substrate, held at a lower temperature than that of the source (e.g., at 1100 C), to initiate the growth of silicon nanowires and nanoparticles.

After completion of the growth process, the silicon structures can be soaked in a solution of hydrofluoric acid (HF) having a concentration of about 10% to remove oxide layers, if there are such layers, and obtain silicon crystal silicon nanowires and nanoparticles. Scanning electron microscopy (SEM) images of prototype silicon structures formed according to the above procedure show a plurality of substantially uniform-sized silicon nanoparticles and a plurality of nanowires formed between adjacent nanoparticles. And selected area electron diffraction (SAED) spectra show that the nanoparticles are composed of a crystalline core and an amorphous outer layer. Application of a HF solution having a selected concentration, e.g., about 10%, to these silicon-knotted nanowires can result in obtaining free-standing silicon nanoparticles. Alternatively, the silicon nanowires can be utilized.

Segmented and coaxial nanowires constitute other building blocks needed for synthesizing nanocomposite compositions according to some embodiments of the invention, such as the compositions 26 and 36 described above. Various techniques are known in the art for generating such nanowires. For example, in order to synthesize segmented nanowires having Si and Ge segments, a vapor phase deposition system, such as the above system 46, with a Si source and a Ge source can be employed. The sources can be activated in an alternating fashion to deposit segmented nanowires on a substrate placed downstream of the sources. In another example, PbSe/PbTe segmented nanowires can be fabricated via electrodeposition onto an alumina (Al_2O_3) template. Aqueous deposition baths having lead acetate as a source for lead, and SeO_2 and TeO_2 as sources of selenium and tellurium, respectively, can be employed. The alumina template can be transferred back and forth between the two corresponding deposition baths, and the deposition potentials can be cycled accordingly. For generating coaxial wires, once nanowires of one type, e.g., silicon, are formed on the substrate in a manner described above, the other source, e.g., a Ge source, can be activated to coat the first wires with a shell, e.g., a shell of Ge.

In one exemplary method according to the teachings of the invention, the nanoparticles and the nanowires are compacted at an elevated temperature and under compressive pressure to synthesize a nanocomposite composition, such as those described above. By way of example, a plasma pressure compaction apparatus 52, schematically depicted in FIG. 10, can be employed for this purpose. Two graphite pistons 54 and 56 apply a high compressive pressure, e.g., a pressure in a range of about 10 to about 1000 MegaPascals (MPa), to a nanoparticles mixture disposed within a graphite cylinder 58, while a current source 60 provides a current density flow through the mixture for heating thereof. In many embodiments, the current density is in a range of about 1000 A/cm² to about 2000 A/cm². The temperature of the mixture, or an estimate thereof, can be obtained by measuring, for example, the temperature of the graphite cylinder via an optical pyrometer (not shown) or a thermocouple attached to the sample surface. The temporal duration of the applied pressure as well as the temperature of the mixture while under pressure are selected so as to cause formation of a nanocomposite composition of interest while inhibiting formation of a homogeneous alloy consisting of the semiconductor components in the mixture.

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For example, for forming a nanocomposite material comprising Si inclusions in a Ge host and one consisting of a mixture of Si and Ge nanoparticles, a powder mixture of Si and Ge nanoparticles can be placed under a compressive pressure of about 127 MPa while flowing a current through the powder. The current can be increased in steps of 200 A every two minutes until the temperature of the mixture reaches about 85° C. The mixture is then held at this temperature under the compressive pressure for about 5 minutes, and subsequently cooled down, e.g., via water cooling of the pistons, over a period of 1 to 2 minutes. Typically, for generating Si/Ge nanocomposites, the temperature of the mixture under pressure is held below the melting temperature of germanium.

By way of example and to illustrate the efficacy of the above methods for generating thermoelectric nanocomposite materials according to the teachings of the invention, FIG. 11 presents X-ray diffraction data corresponding to two prototype nanocomposite samples, herein designated as samples A and B, generated by incorporating nano-sized silicon inclusions in a germanium host matrix in comparison with similar data for a silicon sample, a germanium sample, and a sample composed of a powder mixture of silicon and germanium. This exemplary data provides clear evidence of two compositions within the nanocomposite samples.

Thermoelectric nanocomposite materials of the invention can advantageously find applications in both refrigeration and power generation. For example, they can be utilized in thermal management of microelectronics and photonic devices. Further, they can be employed as thermoelectric power generators for direct conversion of thermal energy to electrical energy at a high efficiency. By way of example, FIG. 12 schematically depicts a thermoelectric cooler 60 formed as an assembly of thermoelectric elements, such as modules 62 and 64. The elements are electrically connected in series (or a combination of serial and parallel connections depending on the needs and power supplies) with current flowing alternatively through p-type and n-type legs (formed of doped nanocomposites of the invention). The legs of the devices are connected through electrically conductive bridges to adjacent legs in a cascading fashion. Application of a current through the modules causes transfer of heat from one side of the thermoelectric cooler to the other, thereby lowering the temperature at one side while increasing the temperature at the opposed side.

Alternatively, as shown in FIG. 13, heat can be applied to one side of a thermoelectric device 66 having n-type and p-type portions—connected via an electrically conductive bridging segment—to generate an electrical voltage across those portions.

Those having ordinary skill in the art will appreciate that various modifications can be made to the above embodiments without departing from the scope of the invention.

What is claimed is:

1. A method of synthesizing a thermoelectric nanocomposite semiconductor composition, comprising
 - generating a powder mixture comprising two or more sets of nano-sized semiconductor structures, and
 - applying a compressive pressure to said mixture while heating the mixture to a selected temperature for a time

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duration selected to cause compaction of said sets of nano-sized structures into the thermoelectric nanocomposite semiconductor composition having a matrix with nano-sized inclusions.

2. The method of claim 1, wherein said compressive pressure is in a range of about 10 to about 1000 MPa.

3. The method of claim 1, wherein said nano-sized structures are semiconductor nanoparticles and the semiconductor nanoparticles of one set have a different composition from the semiconductor nanoparticles of another set.

4. The method of claim 1, wherein the nano-sized inclusions have a size of 1-300 nm.

5. The method of claim 4, wherein the nano-sized inclusions have a size of 1-100 nm.

6. A method of synthesizing a thermoelectric nanocomposite semiconductor composition, comprising

generating a powder mixture comprising two or more sets of nano-sized semiconductor structures, and

applying a compressive pressure to said mixture while heating the mixture to a selected temperature for a time duration selected to cause compaction of said sets of nano-sized structures into the thermoelectric nanocomposite semiconductor composition,

wherein said compressive pressure and said time duration are selected to substantially inhibit formation of a homogenous alloy composed of materials forming said nano-sized structures while facilitating formation of the nanocomposite semiconductor composition.

7. The method of claim 6, wherein said compressive pressure is in a range of about 10 to about 1000 MPa.

8. The method of claim 6, wherein said nano-sized structures are semiconductor nanoparticles and the semiconductor nanoparticles of one set have a different composition from the semiconductor nanoparticles of another set.

9. A method of generating a thermoelectric nanocomposite semiconductor composition, comprising:

generating a powder mixture comprising at least two sets of nanoparticles, wherein at least one set is formed of a host semiconductor material and at least another set is formed of an inclusion semiconductor material, and

applying a compressive pressure to said mixture while heating the mixture to a selected temperature so as to cause compaction of said mixture into the thermoelectric nanocomposite semiconductor composition having said inclusion nanoparticles distributed in a host matrix formed of said host semiconductor material, wherein said inclusion particles in the nanocomposite are nano-sized.

10. The method of claim 9, wherein said compressive pressure is in a range of about 10 to about 1000 MPa.

11. The method of claim 9, wherein the host semiconductor material is different from the inclusion semiconductor material.

12. The method of claim 9, wherein the nano-sized inclusion particles have a size of 1-300 nm.

13. The method of claim 12, wherein the nano-sized inclusion particles have a size of 1-100 nm.

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